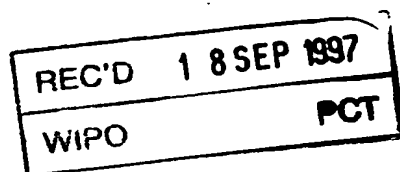


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PCT/US 977-12540
RO/US 26 AUG 1997



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PRIORITY DOCUMENT

I, DAVID DANIEL CLARKE, ASSISTANT DIRECTOR PATENT SERVICES, hereby certify that the annexed are true copies of the Provisional specification and drawing(s) as filed on 18 July 1996 in connection with Application No. PO 1109 for a patent by COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION and E.I. DU PONT DE NEMOURS AND COMPANY filed on 18 July 1996.

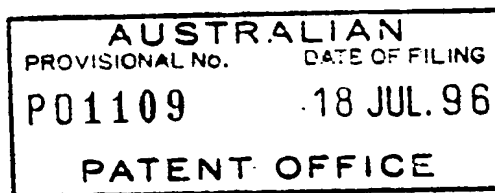
I further certify that the annexed documents are not, as yet, open to public inspection.

WITNESS my hand this Thirtieth
day of July 1997

A handwritten signature in cursive script, appearing to read "D Clarke".

DAVID DANIEL CLARKE
ASSISTANT DIRECTOR PATENT SERVICES





Commonwealth Scientific and Industrial Research Organisation AND
E.I. du Pont de Nemours and Company

A U S T R A L I A
Patents Act 1990

PROVISIONAL SPECIFICATION
for the invention entitled:

Polymerization with Living Characteristics

The invention is described in the following statement:

POLYMERIZATION WITH LIVING CHARACTERISTICS

This invention relates to a free radical polymerization process with characteristics of a living polymerization system in that it is capable of producing polymers of pre-determined molecular weight with narrow molecular weight distribution (low polydispersity), and, by successively adding different monomers, can be used to make block copolymers with low polydispersity. The process can be used to produce polymers of more complex architecture, including variously branched homo- and copolymers. The use of certain reagents in this process and the polymers produced are also claimed.

There is increasing interest in methods for producing a variety of polymers with control of the major variables affecting polymer properties. Living polymerizations provide the maximum degree of control for the synthesis of polymers with predictable well defined structures. The characteristics of a living polymerization are discussed by Quirk and Lee (*Polymer International* 27, 359 (1992)) who give the following experimentally observable criteria:

1. Polymerization proceeds until all of the monomer has been consumed; further addition of monomer results in continued polymerization.
2. The number average molecular weight (or the number average degree of polymerization) is a linear function of conversion.
3. the number of polymer molecules (and active centers) is a constant which is sensibly independent of conversion.
4. The molecular weight can be controlled by the stoichiometry of the reaction.
5. Narrow molecular weight distribution (low polydispersity) polymers are produced.
6. Block copolymers can be prepared by sequential monomer addition.
7. Chain end-functionalized polymers can be prepared in quantitative yield.

Thus living polymerizations produce polymers of narrow molecular weight distribution containing one or more monomer sequences whose length and composition are controlled by the stoichiometry of the reaction and the degree of conversion. Homopolymers, random copolymers or block copolymers may be produced with a high degree of control and with low polydispersity.

Reversible chain transfer systems

Swarc (*Adv. Polym. Sci.* **49**, 1 (1983)) stated that living polymerization to give polymers of narrow molecular weight distribution requires the absence of chain transfer and termination reactions, the elementary reactions being only initiation and propagation, which take place uniformly with respect to all growing polymer chains. Later Inoue and Aida in an article on living polymer systems (*Encyclopedia of Polymer Science and Engineering*, Supplement Volume, Wiley Interscience New York 1989) stated "If chain transfer and terminating agents are present in the polymerization system the living character of the polymerization is lost, and the formation of polymer with narrow molecular weight distribution does not result."

In a theoretical study based on polymerization kinetics of ideal systems, Matyjaszewski (*Polymer Preprints*, **37**(1), 325 (1996)) analyzed approaches to controlled/"living" carbocationic and free radical polymerization systems using the concept of reversible activation of dormant species. He proposed that the most important parameter in controlling molecular weights and polydispersities in systems with equilibria between dormant and propagating species is the relative rate of deactivation versus propagation, ie. with increasing number of monomer molecules added during each activation period polydispersities increase and control is lost. In another theoretical paper (*Makromol. Chem. Macromol Symp.*, **47**, 315 (1991)) Matyjaszewski relates polydispersity at complete conversion to the number of monomer units which are incorporated at a single activation period (λ) and the final degree of polymerization (DP_n) in the equation:

$$\bar{M}_w/\bar{M}_n = 1 + \lambda/DP_n$$

λ is influenced by many factors including the instantaneous concentration of monomer, the concentration of dormant species, the temperature - any or all of which may change during the course of a real polymerization - and also by the rate constants associated with propagation and the activation/deactivation equilibria. In a real polymerization, side reactions and termination reactions may influence the composition of the final product as can adventitious chain transfer.

In the case of systems with reversible chain transfer a short activation period and low λ are most readily obtained when the dormant species (for example, AR and AP_n in Scheme 1) have high chain transfers constants.

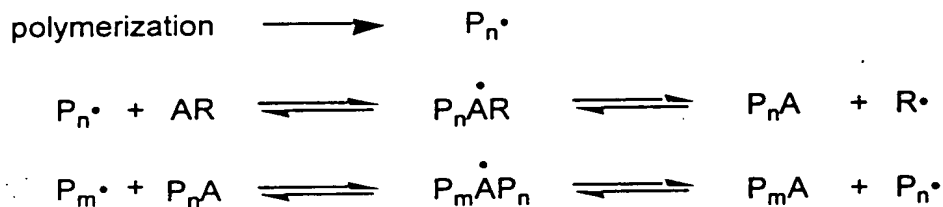
Block copolymer syntheses in the presence of certain dithiocarbamates as initiator-transfer agents have been described. In these examples the dithiocarbamate is used as a photochemical initiator and the chemistry involves formation of sulfur-centered radicals. For a discussion of this chemistry see recent reviews [Moad *et al.* in *Comprehensive Polymer Science*; Pergamon: London, vol 3, p 141 (1989); Nair *et al.*, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C31**, 311 (1991)]. These dithiocarbamates (for example, benzyl dithiocarbamate) have low transfer constants and are ineffective in the context of the current invention. The art is not successful in producing low polydispersity polymers and does not give high purity block copolymers. Greszta *et al.* (*Macromolecules*, **27**, 638 (1994)) have described the application of chain transfer chemistry in living radical

polymerization and have proposed and rejected the use of dithiocarbamates in this context because of the problem of side reactions.

We have now discovered that free radical polymerizations carried out in the presence of certain addition-fragmentation chain transfer agents and with appropriate choice of reaction conditions have living characteristics and can provide polymers of controlled molecular weight and very low polydispersity. With appropriate choice of chain transfer agent the process may be used for the synthesis of low polydispersity block, star, or graft copolymers.

While not wishing to be limited to any particular mechanism, it is believed that the mechanism of the process is as summarized in Scheme 1 below. Propagating radicals P_n^\bullet are produced by radical polymerization. These can react reversibly with the chain transfer agent AR to form an intermediate radical $P_nA(\bullet)R$ which fragments to give a radical R^\bullet (which adds monomer to reinitiate polymerization) and a new transfer agent P_nA . This new transfer agent P_nA has similar characteristics to the original transfer agent AR in that it reacts with another propagating radical P_m^\bullet to form an intermediate radical $P_nA(\bullet)P_m$ which fragments to regenerate P_n^\bullet and form a new transfer agent P_mA which again has similar characteristics to AR. This process provides a mechanism for chain equilibration and accounts for the polymerization having living characteristics.

Scheme 1:



P_n^\bullet and P_m^\bullet are propagating radicals of chain length n and m respectively.

R^\bullet is a chain transfer agent derived radical which can initiate polymerization to produce a new propagating radical.

AR, P_nA and P_mA are chain transfer agents which react by an addition-fragmentation mechanism.

A Japanese patent application (JP 04198303 A2) has described polymerization in the presence of triarylmethyl dithiocarboxylates $[Ar_3CSC(S)R]$ as initiators of polymerization to yield block copolymers which may have low polydispersity (all examples have $\bar{M}_w/\bar{M}_n \geq 1.4$). These compounds have a very weak carbon-sulfur bond that cleaves under polymerization conditions to give a stable triarylmethyl radical $[Ar_3C^\bullet]$ and a

thiocarbonylthiyl radical $[RC(S)S^{\bullet}]$. They are likely to be poor chain transfer agents in the context of the present invention.

Rizzardo *et al.* (*Macromol. Symp.* **98**, 101 (1995)) review polymerization in the presence of addition-fragmentation chain transfer agents but do not mention the possibility of low polydispersity products.

Polymers or oligomers with a vinyl terminal group are known as macromonomers. Macromonomers which are addition-fragmentation chain transfer agents are disclosed in *J. Macromol. Sci.- Chem.* **A23**, 839 (1986) and International Patent publications WO 93/22351 and WO 93/22355. Free radical polymerization with living characteristics utilizing these macromonomers as chain transfer agents is disclosed in International Patent Application PCT/US95/14428.

The process of this invention has advantages over the process of PCT/US95/14428 in that it is compatible with a wider range of monomers and reaction conditions and will generally give improved control over molecular weight, molecular weight distribution, ie polydispersity, and polymer architecture.

Accordingly this invention provides a free radical polymerization process with living characteristics, which process comprises polymerizing one or more monomers in the presence of a source of free radicals and a chain transfer agent (CTA), which CTA during the polymerization reacts with the initiating or propagating radical and following such reaction reversibly fragments to give a radical capable of initiating polymerization and another CTA with similar characteristics to the original CTA; the reaction conditions being chosen so that the ratio of the total number of initiator-derived radicals to the number of chain transfer agent molecules is maintained at a minimum value consistent with achieving an acceptable rate of polymerization, preferably less than 0.1, and the chain transfer constants of the CTAs are greater than 0.1, preferably greater than 1, and more preferably, greater than 10.

The invention represents a significant advancement in polymer synthesis. All of the benefits which derive from the use of radical polymerization can now be realized in syntheses of low polydispersity homo- and copolymers. The ability to synthesize block, graft, star and end-functional polymers and copolymers further extends the value of the process. The general concept is applicable to a wide range of monomers. There are substantial cost improvements over alternate technologies which involve other polymerization mechanisms (*e.g.* group transfer polymerization, anionic polymerization) which require more stringent control of monomer purity and are not compatible with protic monomers or protic solvents.

The source of free radicals may be any suitable method of generating free radicals such as the thermally induced homolytic scission of peroxides, peroxyester, or azo compounds, the spontaneous generation from monomer (*e.g.* styrene), redox initiating systems, photochemical initiating systems, or high energy radiation such as electron beam, X- or γ -radiation. The initiating system is chosen such that under the reaction conditions there is no adverse interaction of the initiator or the initiating radicals with the transfer agent. The

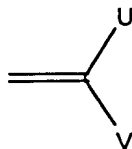
non-radiation initiators are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate half life at the temperature of polymerization; these initiators include one or more of the following compounds:

2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-butanenitrile), 4,4'-azobis(4-cyanopentanoic acid), 1,1'-azobis(cyclohexane-carbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis[2-methyl-N-(1,1)-bis(hydroxymethyl)-2-hydroxyethyl]propionamide, 2,2'-azobis[2-methyl-N-hydroxyethyl]propionamide, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dichloride, 2,2'-azobis(2-amidinopropane) dichloride, 2,2'-azobis(N,N'-dimethyleneisobutyramide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide), 2,2'-azobis(2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide), 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(isobutyramide) dihydrate, t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyoctoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxy-pivalate, t-butyl peroxy-pivalate, di-isopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, potassium persulfate, ammonium persulfate.

Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995.

Initiating radicals are radical species derived from the initiator or other species which add monomer to produce propagating radicals. Propagating radicals are radical species that have added one or more monomer units and are capable of adding further monomer units (for definition see Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995)

The process of the invention may be applied to any polymerizable monomers or monomer combinations which are susceptible to free radical polymerization. Such monomers include those with the general structure:



where U is hydrogen, halogen, R", OR", or O₂CR";

V is hydrogen, phenyl, aryl, R", optionally substituted alkenyl, COR", CO₂H, CO₂R", CN, CONH₂, CONHR", CONR"₂, O₂CR", or halogen;

R" is optionally substituted alkyl.

Monomers CH₂=CUV as used herein include acrylate and methacrylate esters, acrylic and methacrylic acid, styrene, acrylamide, methacrylamide, and methacrylonitrile, mixtures of these monomers, and mixtures of these monomers with other monomers. As one skilled in

the art would recognize, the choice of (co)monomers is determined by the steric and electronic properties of the monomer.

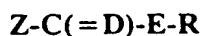
Compounds suitable as monomers or comonomers include the following:

methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha methyl styrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates, acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-tert-butyl methacrylamide, N-n-butyl methacrylamide, N-methylol methacrylamide, N-ethylol methacrylamide, N-tert-butyl acrylamide, N-n-butyl acrylamide, N-methylol acrylamide, N-ethylol acrylamide, vinyl benzoic acid (all isomers), diethylamino styrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers), p-vinyl benzene sulfonic acid, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethyl-silylpropylmethacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, and vinyl butyrate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride.

Other suitable monomers include cyclopolymerizable monomers such as those disclosed in International Patent Application PCT/AU94/00433.

To be useful in this invention chain transfer agents must undergo chain transfer by an addition-fragmentation mechanism.

Suitable CTAs are those compounds of Formula 1 below with a "reactively symmetrical" structure.

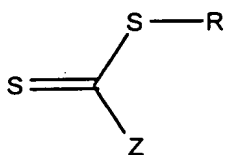


(Formula 1)

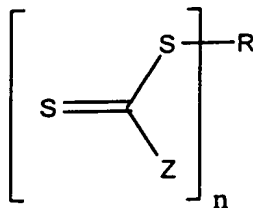
By "reactively symmetrical structure" is meant one where the chain transfer activity of $Z-C(=D)-E-R$ is similar to that of $Z-C(=E)-D-R$. The groups R and Z are defined below. The groups denoted by D and E may be the same or different and may be selected from sulphur or CQ_2 where Q is chosen so that the group CQ_2 is susceptible to free radical addition. The two Q groups may be the same or different and are chosen from hydrogen

and fluorine. Compounds of Formula 1 where D and E are both CH_2 and R is a polymer chain are known as macromonomers. The use of these macromonomers as CTAs in polymerization processes is not part of this invention.

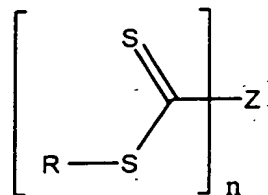
Preferred chain transfer agents of Formula 1 are those where both D and E are sulfur atoms ie Formulae 1a to 1c below.



Formula 1a



Formula 1b



Formula 1c

WHERE:

In Formula 1a:

Z is a group chosen such that the chain transfer constant is in the desired range (as defined above), suitable Z groups are hydrogen or optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxy, optionally substituted alkylthio, chlorine, optionally substituted alkoxycarbonyl or optionally substituted aryloxycarbonyl ($-\text{COOR}$), carboxy ($-\text{COOH}$), optionally substituted acyloxy ($-\text{O}_2\text{CR}$), optionally substituted carbamoyl ($-\text{CONR}_2$), or cyano ($-\text{CN}$); or a polymer chain;

R is an optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring, or optionally substituted alkylthio, or other group such that R^\bullet is a free radical leaving group under the polymerization conditions and is capable of initiating free radical polymerization. R may also be a polymer chain prepared by any polymerization mechanism or an organometallic species.

In Formula 1b:

n is an integer greater than 1.

R is a group derived from optionally substituted alkyl, optionally substituted aryl or a polymer chain, or other group such that R• is a free radical leaving group under the polymerization conditions and is capable of initiating free radical polymerization; and

Z is as defined for Formula 1a.

In Formula 1c:

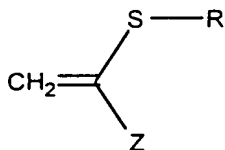
n is an integer greater than 1.

Z is a group derived from optionally substituted alkyl, optionally substituted aryl or a polymer chain where the connecting moieties are selected from aliphatic carbon, aromatic carbon, oxygen or sulfur; and

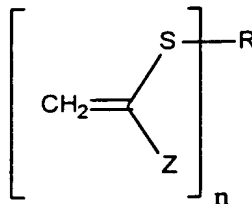
R is as defined for Formula 1a.

Compounds of Formula 1b, or 1c may be used to produce branched homo- or co- polymers with the number of arms being less than or equal to n.

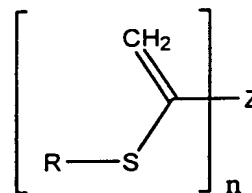
Another group of chain transfer agents suitable for use in the process of this invention are the compounds of Formula 1d to 1i below.



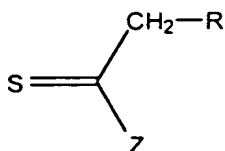
Formula 1d



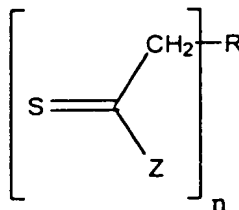
Formula 1e



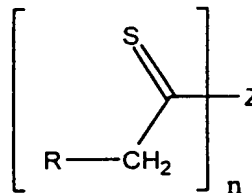
Formula 1f



Formula 1g



Formula 1h



Formula 1i

WHERE:

In Formula 1d or 1g:

Z is a group chosen such that the chain transfer constant is in the desired range, suitable Z groups are hydrogen or optionally substituted alkyl, optionally substituted aryl, optionally substituted alkoxy, optionally substituted alkylthio optionally substituted alkoxy carbonyl or optionally substituted aryloxy carbonyl (-COOR), carboxy (-COOH), optionally substituted acyloxy (-O₂CR), optionally substituted carbamoyl (-CONR₂), or cyano (-CN) or a polymer chain prepared by any polymerization mechanism;

R is an optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring or may be a polymer chain; R being chosen such that R• is a free radical leaving group under the polymerization conditions and is capable of initiating free radical polymerization.

In Formula 1e or 1h:

n is an integer greater than 1.

R is derived from an optionally substituted alkyl, optionally substituted aryl, a polymer chain, or other group such that R• is a free radical leaving group under the polymerization conditions and is capable of initiating free radical polymerization; and

Z is as defined for Formula 1d.

In Formula 1f or 1i :

n is an integer greater than 1.

Z is derived from an optionally substituted alkyl, optionally substituted aryl or a polymer chain, where the connecting moieties are selected from aliphatic carbon, aromatic carbon, oxygen or sulfur; and

R is as defined for Formula 1d.

Compounds of Formula 1e, 1f, 1h or 1i can be used to produce branched polymers with the number of arms being less than or equal to n.

In the compounds of general formula 1 or specific formulae 1a - 1i, substituted rings may have reactive substituent groups directly or indirectly attached to the ring by means of a methylene group or other side chain.

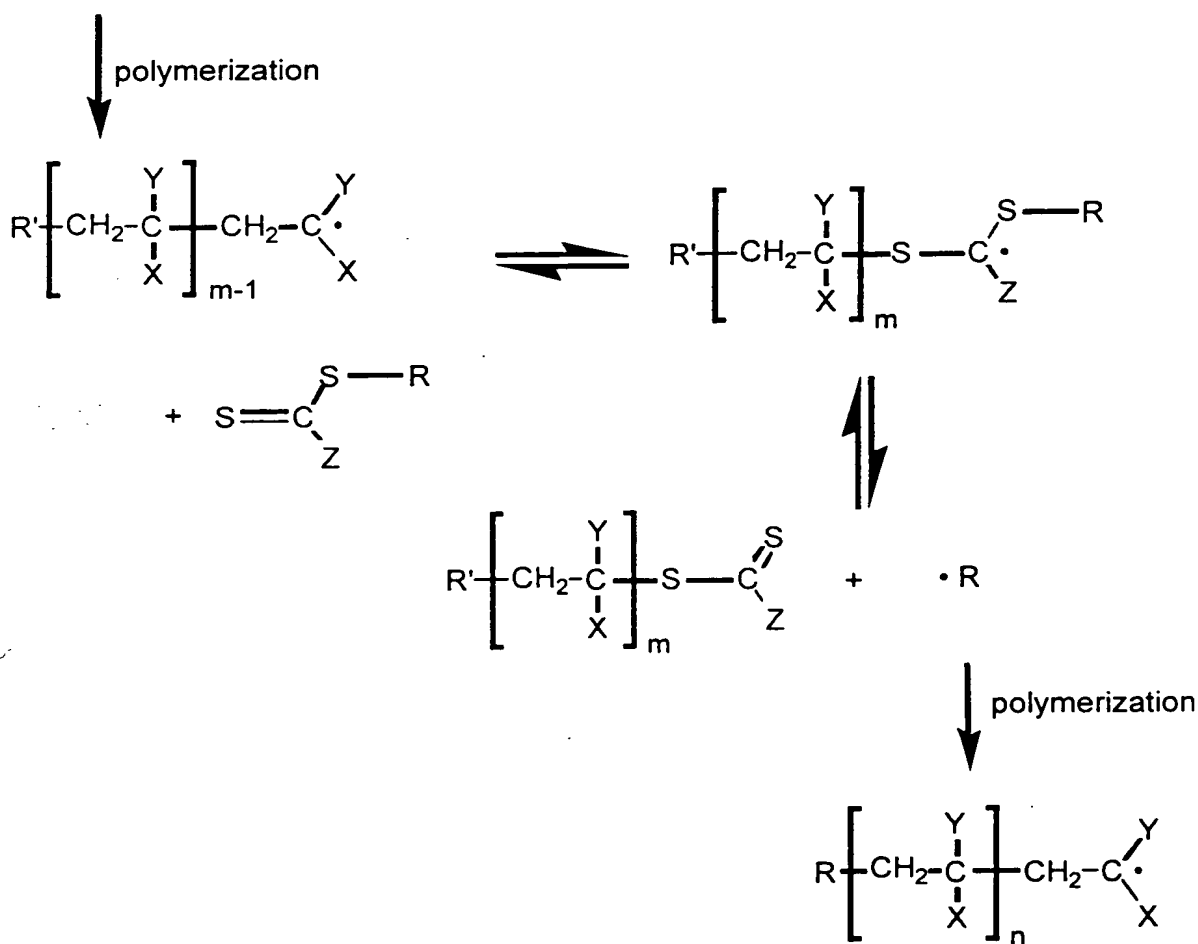
The substituents on groups referred to above for R and/or Z in formula 1 do not take part in the polymerization reactions but form part of the terminal groups of the polymer chains and may be capable of subsequent chemical reaction. The low polydispersity polymer containing any such reactive group is thereby able to undergo further chemical

transformation, such as being joined with another polymer chain. Suitable reactive substituents include: hydroxy (-OH); amino (-NH₂); halogen; cyano; epoxy; and carboxylic acid (-COOH) and its derivatives, such as ester (-COOAlkyl). Alternatively, the substituents may be non-reactive such as alkoxy, alkyl or aryl.

Alkyl groups referred to in this specification may contain from 1 to 32 carbon atoms. Alkenyl and alkynyl groups may contain from 2 to 32 carbon atoms. Saturated, unsaturated, or aromatic carbocyclic or heterocyclic rings may contain from 3 to 14 atoms.

An example of the preferred class of chain transfer agents are the dithioesters (Formula 1a) such as are depicted in Scheme 2 which is illustrative of the reaction mechanism believed to be operative in the process of this invention. It should be understood however, that the invention is not limited to the mechanism depicted and that other mechanisms may be involved.

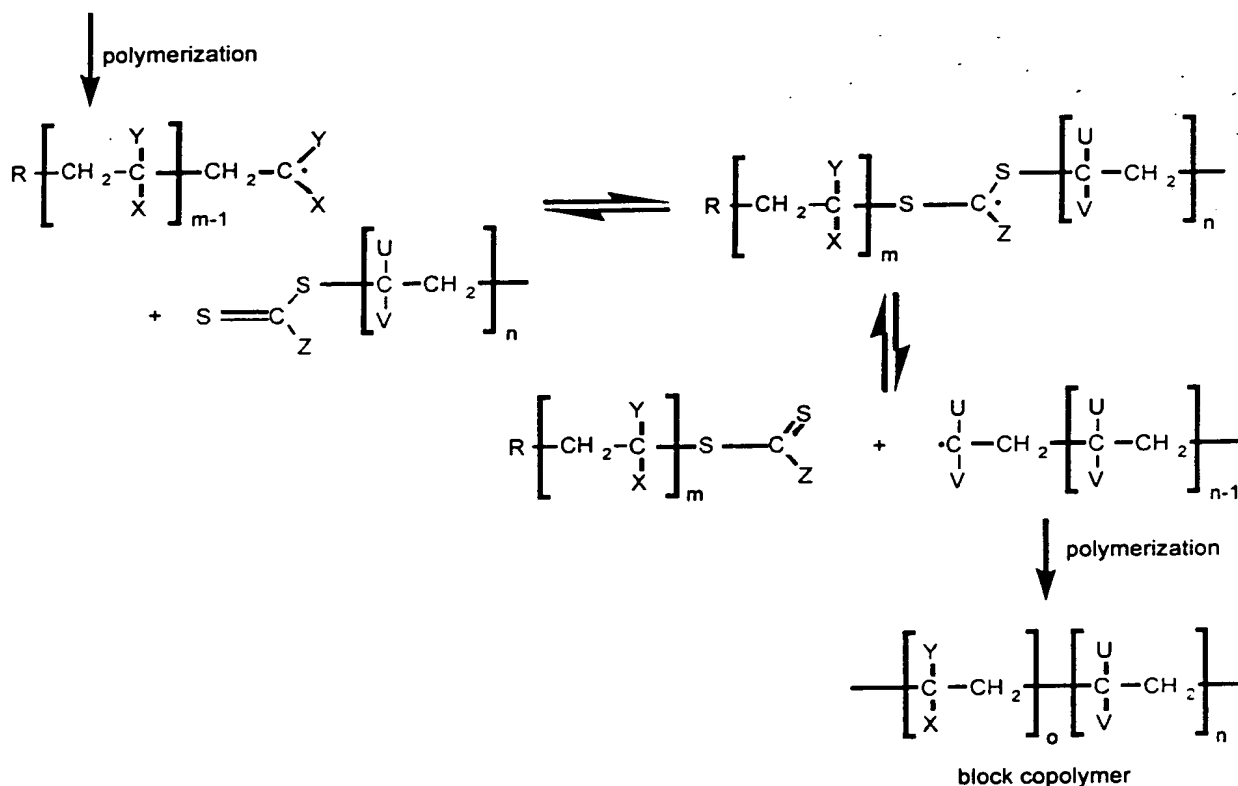
Scheme 2:



R and R' are fragments derived from initiating or propagating radicals

A key feature of the invention is the retention of the active end group in the polymeric product. The invention thus also provides a route to block copolymers as illustrated, for example, in Scheme 3.

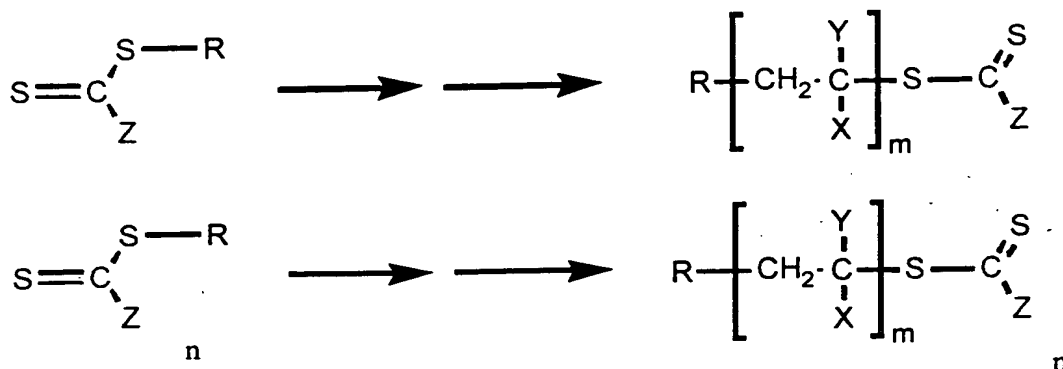
Scheme 3:



R is a fragment derived from an initiating or a propagating radical

As mentioned above, polymers with more complex architectures including multiblock, star and graft copolymers are available through the use of reagents containing multiple groupings. Scheme 4 illustrates this.

Scheme 4:



It will be obvious that other structures capable of giving addition-fragmentation chain transfer and of meeting the requirement for being "reactively symmetrical" will also be effective in this invention. This includes compounds analogous to $Z-C(=D)-E-R$ or $Z-C(=E)-D-R$ but where the unsaturated linkage [$C(=D)-E$ or $C(=E)-D$] and the radical leaving group R are separated by a conjugating linkage, for example a double bond.

Benefits of the polymerization process described in this invention are:

- a) Low polydispersity polymers and copolymers can be synthesized

In the context of the present invention, low polydispersity polymers are those with polydispersities that are significantly less than those produced by conventional free radical polymerization. In conventional free radical polymerization polydispersities (\bar{M}_w/\bar{M}_n) of the polymers formed are typically in the range 1.6-2.0 for low conversions (<10%) and may be substantially greater than this for higher conversions. Polydispersities obtained with the present invention are usually less than 1.5 and, with appropriate choice of the transfer agent and the reaction conditions, may be less than 1.2. The low polydispersity is maintained at high conversions (see examples).

Note that it is also possible to produce polymers with broad, yet controlled, polydispersity or multimodal molecular weight distribution by controlled addition of the CTA over the course of the polymerization process.

- b) Molecular weights increase in a predictable and linear manner with conversion (see Example 1) which is dependent on the stoichiometry.

In the case of monofunctional CTAs, the degree of polymerization (DP_n) of the product can be calculated according to the relationship:

$$DP_n(\text{product}) = \frac{[\text{moles monomer consumed}]}{[\text{moles CTA}]} + DP_n(\text{CTA})$$

This expression applies under the typical reaction conditions which require that the number of initiator-derived chains is negligible.

- c) The methodology can be applied to provide low polydispersity:
- End-functional polymers and copolymers
 - Block and multiblock and gradient copolymers
 - Star polymers
 - Graft or branched copolymers.
- d) The methodology is compatible with a wider range of monomers and reaction conditions when compared to other processes for producing low polydispersity and reactive polymers.

Specific advantages of the present process over that with the macromonomer CTAs as disclosed in PCT/US95/14428 are:

- i) The much higher transfer constant of compounds of Formula 1 (transfer constant can be >20) in comparison to macromonomers (transfer constant <2) means that it is not necessary to use starved-feed conditions to obtain narrow polydispersity polymers or block copolymers. It is possible to use a batch polymerization process (see examples).
- ii) The compounds of Formula 1 do not readily undergo copolymerization with monomers. Therefore, narrow polydispersity polymers based on monosubstituted monomers (e.g. acrylic monomers, styrene) can be carried out under a wider range of reaction conditions. The macromonomers disclosed in PCT/US95/14428 may give graft copolymers when polymerized in the presence of monosubstituted monomers at low reaction temperatures $<100^{\circ}\text{C}$.

The choice of the CTA compound is important in synthesis of low polydispersity polymers. The preferred dithioesters and related compounds give chain transfer (by an addition-fragmentation mechanism) and have very high chain transfer constants.

Four factors influence the effectiveness of the CTA in the process of this invention:

- a) The rate of reaction of the CTA (AR and AP_n in Scheme 1).
- b) The partitioning of the intermediate radicals ($\text{P}_n\text{A}^{\bullet}\text{R}$ and $\text{P}_n\text{A}^{\bullet}\text{P}_m$ in Scheme 1) between starting materials and products.
- c) The rate of fragmentation of the intermediate radicals ($\text{P}_n\text{A}^{\bullet}\text{R}$ and $\text{P}_n\text{A}^{\bullet}\text{P}_m$ in Scheme 1).
- d) The ability of the expelled radicals (R^{\bullet} and P_n^{\bullet} in Scheme 1) to reinitiate polymerization.

Factors a) and b) determine the transfer constant of the CTA compound. The transfer constant is defined as the ratio of the rate constant for chain transfer to the rate constant for

propagation at zero conversion of monomer and CTA compound. Preferably the transfer constant for the addition-fragmentation chain transfer process is >0.1 . The polydispersity obtained under a given set of reaction conditions is sensitive to the value of the transfer constant. Lower polydispersities will result from the use of reagents with higher transfer constants. Benzyl dithiobenzoate derivatives have transfer constants which are >20 in polymerization of styrene or arylate esters. Higher transfer constants also allow greater flexibility in the choice of reaction conditions. For reagents with low chain transfer constants, the use of feed addition is advantageous to obtain low polydispersities.

We have discovered that the chain transfer activity of dithiocompounds of Formula 1a is a function of the substituents R and Z and the propagating radical. R should be chosen so as to be a free radical leaving group under the polymerization conditions (and yet retain ability to reinitiate polymerization - see below). Z should be chosen to activate the double bond towards addition (whilst not slowing the rate of fragmentation to the extent that there is an unacceptable retardation of polymerization - see below). For example, the transfer constant increases in the series where $Z = -NMe_2 > OMe > Me > Ph$. The compound where $Z = NMe_2$, $R = CH_2Ph$ has a very low transfer constant (<0.1) and is ineffective, whereas we have found that the compound where $Z = Ph$, $R = CH_2Ph$ has a very high transfer constant (>20 in styrene polymerization) and is effective (see examples).

Factors c) and d) determine whether or not there is retardation of polymerization and the extent of any retardation. If the overall rate of reinitiation is greater than or equal to the rate of propagation there will be no retardation. These factors will be influenced by the substituents R and Z and the nature of the propagating radical.

We have also found that the relative rates of addition and of fragmentation can be estimated using molecular orbital calculations. This method and information on radical reactivities (see for example Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995) will assist those skilled in the art in selecting transfer agents for particular polymerizations.

For heterogeneous polymerization it is desirable to choose a CTA which has appropriate solubility parameters. For aqueous emulsion polymerization the CTA should preferably partition in favour of the organic (monomer) phase and yet have sufficient aqueous solubility that it is able to distribute between the monomer droplet phase and the polymerization locus.

The choice of polymerization conditions is also important. The reaction temperature will influence the rate parameters discussed above. For example, higher reaction temperatures will typically increase the rate of fragmentation.

Conditions must be chosen such that the number of chains formed from initiator-derived radicals is minimized to an extent consistent with still obtaining an acceptable rate of polymerization. Termination of polymerization by radical-radical reaction will lead to chains which contain no active group and therefore cannot be reactivated. The rate of radical-radical termination is proportional to the square of the radical concentration. Furthermore, in the synthesis of block star or branched polymers, chains formed from

initiator-derived radicals will constitute a linear homopolymer impurity in the final product. These conditions require careful choice of the initiator concentration and, where appropriate, the rate of the initiator feed.

It is also desirable to choose other components of the polymerization medium (for example, the solvents, surfactants, additives, and initiator) such that they have a low transfer constant towards the propagating radical. Reaction of propagating radicals by chain transfer to these species will lead to the formation of chains which do not contain the active group.

With these provisos, the polymerization process according to the present invention is performed under the conditions typical of conventional free radical polymerization. Polymerizations employing the above described chain transfer agents is suitably carried out with temperatures during the reaction in the range 10 to 200°C, preferably in the range 40-160°C.

The polymerization process may be carried out in emulsion, solution or suspension in either a batch, semi-batch, continuous, or feed mode. Conventional procedures may be used to produce narrow polydispersity polymers provided that the CTA is added before polymerization is commenced. For example, when carried out in batch mode in solution, the reactor is typically charged with CTA and monomer or medium plus monomer. To the mixture is then added the desired amount of initiator and the mixture is heated for the requisite time - this may range up to ten initiator half lives.

Polymers with broad, yet controlled, polydispersity or multimodal molecular weight distribution can be produced by controlled addition of the CTA over the course of the polymerization process.

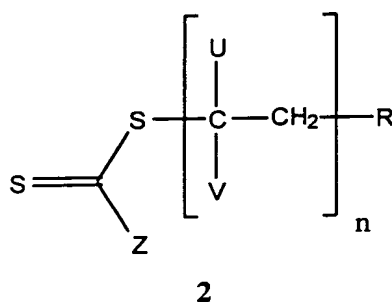
In the case of emulsion or suspension polymerization the medium will often be predominantly water and the conventional stabilizers, dispersants and other additives may be present. For solution polymerization the reaction medium may be chosen from a wide range of organic solvents to suit monomers to be used.

If the polymerization is carried out as a feed system the reaction may be carried out as follows. The reactor is charged with the chosen medium, the CTA and optionally a portion of the monomer(s). Into a separate vessel is placed the remaining monomer(s). Initiator is dissolved or suspended in reaction medium in another separate vessel. The medium in the reactor is heated and stirred while the monomer + medium and initiator + medium are introduced, for example by a syringe pump or other pumping device. The rate and duration of feed is determined largely by the quantity of solution and the desired monomer/CTA/initiator ratio. When the feed is complete, heating may be continued for an additional half hour or more. Examples of feed processes are provided in examples 10, 11 and 17, which follow.

Following completion of the polymerization, the polymer may be isolated by stripping off the medium and unreacted monomer(s) or by precipitation with a non-solvent. Alternatively the polymer solution/emulsion may be used as such, if appropriate to its application.

The invention has wide applicability in the field of free radical polymerization and may be used to produce polymers and compositions having many uses. Such polymers may be used in coatings, including clear coats and base coat finishes or paints for automobiles and other vehicles or maintenance finishes for a wide variety of substrates. Such coatings may further include pigments durability agents, corrosion and oxidation inhibitors, rheology control agents, metallic flakes and other additives. Block and star, and branched polymers may be used as compatibilisers, thermoplastic elastomers, dispersing agents or rheology control agents. Additional applications for polymers of the invention are in the fields of imaging, electronics(eg photoresists), engineering plastics, adhesives, sealants, and polymers in general.

In one aspect this invention provides polymers of general structure (2) and analogous structures based on the use of reagents (1b-g).



where

Z, R are as previously defined

$-\text{[CH}_2\text{CUV]}_n$ is a homo or copolymer chain, where U and V are as defined above, and

n is > 1.

The polymers (2) formed with the use of reagents of formulae (1a) are typically coloured due to the presence of the thiocarbonylthio chromophore $[-\text{C}(=\text{S})\text{S}-]$. The intensity and nature of the colour depends on the concentration of the chromophore and the substituent groups and may range from pale yellow through purple. In the case where white or colourless polymers are required this colour can be removed or lessened by treatment of the polymer with a solution of a suitable oxidising agent or by hydrolysis. Suitable oxidising agents include sodium hypochlorite and t-butyl hydroperoxide. Suitable reagents for effecting hydrolysis include tetramethyl ammonium hydroxide.

The operation of this invention is described in the non-limiting examples given below. The immediately following section describes the structure and preparation of examples of the preferred chain transfer agents applicable in the process.

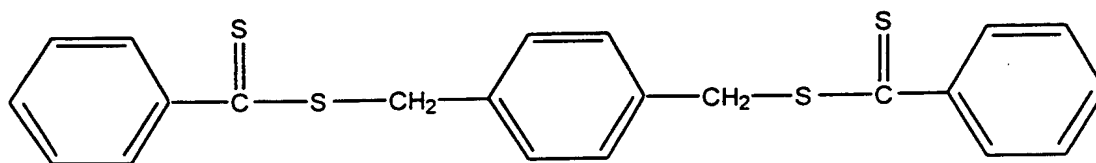
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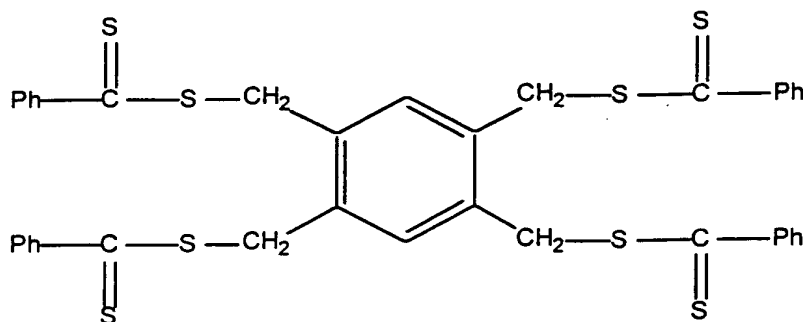
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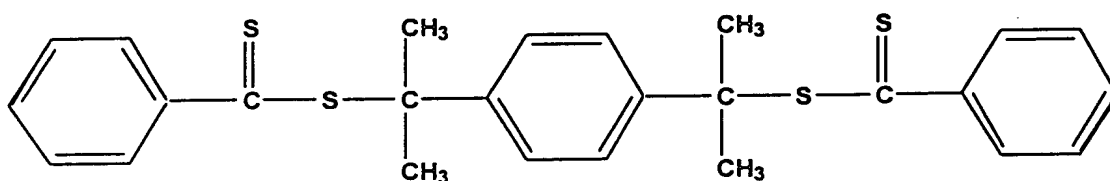
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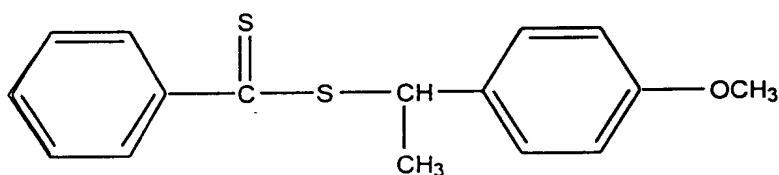
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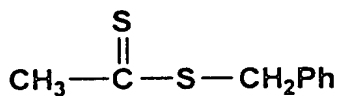
(9)



(10)



(11)



(12)

Preparation of benzyl dithiobenzoate (3)

This material was prepared in a one-pot procedure described in *Recueil*, 92, 601 (1973) for the preparation of methyl- and ethyl dithiobenzoates.

Phenyl Grignard reagent was prepared from bromobenzene (62.8 g, 0.4 mole) and magnesium turnings (10 g) in dry THF (300 mL). The solution was warmed to 40°C and

carbon disulfide (30.44 g, 0.4 mole) was added over 15 minutes whilst maintaining the reaction temperature at 40°C. The resulting mixture turned dark brown. Benzyl bromide (76.95 g, 0.45 mole) was added over 15 minutes. The reaction temperature was raised to 50°C and maintained for further 45 minutes. Ice water (1.5 L) was then added and the organic products were extracted with diethyl ether (total 2 L). The combined organic layers were then washed with water (1 L), brine (500 mL) and dried over anhydrous magnesium sulfate. After removal of solvent and vacuum distillation, the product, benzyl dithiobenzoate, was obtained as a red oil (60.2 g, 61.7% yield), b.p. 152°C (0.02 mmHg) [lit*: b.p. 179-180°C at 3 mmHg]. ¹H-NMR (CDCl₃) δ (ppm): 4.60 (s, 2H); 7.30-7.60 (m, 8H) and 8.02 (m, 2H).

* ref: Beilstein, E III 9, 1998.

Preparation of 1-phenylethyl dithiobenzoate (4)

Dithiobenzoic acid was prepared according to the method of German Patent 1,274,121 (1968); (CA70: 3573v).

Dithiobenzoic acid (9.9 g), styrene (10 mL) and carbon tetrachloride (30 mL) were combined and the mixture heated at 70°C for 4 hours. The yield of 1-phenylethyl dithiobenzoate was 43.4% after purification on an aluminium oxide (activity III) column with petroleum spirit 40-60°C as eluent. ¹H-NMR (CDCl₃) δ (ppm): 1.92 (d, 3H); 5.39 (q, 1H); 7.34-7.62 (m, 8H) and 8.08 (m, 2H).

Preparation of 2-phenylpropyl dithiobenzoate (5)

2-Phenylpropyl dithiobenzoate was prepared from the reaction of dithiobenzoic acid (10.59 g), α-methylstyrene (10 g) and carbon tetrachloride (40 mL) at 70°C for 4 hours. Purification by chromatography on an aluminium oxide column (activity III) using n-hexane as eluent, gave 2-phenylpropyl dithiobenzoate (6.1g, 32.6% yield) as a dark purple oil. ¹H-NMR (CDCl₃) δ (ppm): 2.03 (s, 6H); 7.20-7.60 (m, 8H) and 7.86 (m, 2H).

Preparation of 1-acetoxyethyl dithiobenzoate (6)

1-Acetoxyethyl dithiobenzoate was prepared from the reaction of dithiobenzoic acid (4.0 g), vinyl acetate (10 mL) and carbon tetrachloride (15 mL) at 70°C for 16 hours. Purification by chromatography on an aluminium oxide column (activity III) using n-hexane as eluent gave 1-acetoxyethyl dithiobenzoate (3.21g, 51.5% yield) as a dark red oil. ¹H-NMR (CDCl₃) δ (ppm): 1.80 (d, 3H); 2.09 (s, 3H); 6.75 (q, 1H); 7.34-7.60 (m, 3H) and 7.97 (m, 2H).

Preparation of hexakis-(dithiobenzoylmethyl)benzene (7)

Hexakis-(dithiobenzoylmethyl)benzene was prepared from hexakis(bromomethyl)benzene in a manner analogous to that described above for benzyl dithiobenzoate. The reaction was kept at 50°C for 3 hours. After the usual work-up, recrystallization from 1:3 chloroform/ethanol gave the title compound (7) as a red solid (77% yield), m.p. 222-224°C (dec). $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 4.66 (s, 12H); 7.30-7.60 (m, 18H) and 7.94 (m, 12H).

Preparation of 1,4-bis-(dithiobenzoylmethyl)benzene (8)

1,4-Bis-(dithiobenzoylmethyl)benzene was prepared from a,a'-dibromo-p-xylene in a manner analogous to that described above for benzyl dithiobenzoate. The reaction was kept at 40°C for 1.5 hours. After the usual work-up, recrystallization from EtOH gave the title compound as a red solid (66.7% yield), m.p. 95-97°C. $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 4.60 (s, 4H); 7.34-7.60 (m, 6H) and 8.00 (m, 4H).

Preparation of 1,2,4,5-tetrakis-(dithiobenzoylmethyl)benzene (9)

1,2,4,5-Tetrakis-(dithiobenzoylmethyl)benzene was prepared from 1,2,4,5-tetrakis-(bromomethyl)benzene in a manner analogous to that described above for benzyl dithiobenzoate. The reaction was kept at 40°C for one hour. The usual work-up gave a red solid which was recrystallized from 1:4 benzene/EtOH to give 1,2,4,5-tetrakis-(dithiobenzoylmethyl)benzene (% yield), m.p. 142-143.5°C (dec). $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 4.65 (s, 8H); 7.30-7.58 (m, 14H) and 7.97 (m, 8H).

Preparation of 1,4-bis-(dithiobenzoylprop-2-yl)benzene (10)

1,4-diisopropenylbenzene (3.96 g) was added to a solution of dithiobenzoic acid (8 g) in carbon tetrachloride (50 mL) and the mixture heated at 70°C for 16 hours. Removal of the solvent, gave a thick purple syrup. Trituration with 1:2 diethyl ether: n-hexane allowed isolation of the title compound as a purple solid (2.87 g, 24.6% yield), m.p. 143-145°C (dec). $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 2.00 (s, 12H); 7.33 (m, 4H); 7.49 (m, 2H); 7.50 (s, 4H) and 7.86 (m, 4H).

Preparation of 1-(4-methoxyphenyl)ethyl dithiobenzoate (11)

Dithiobenzoic acid was prepared according to the method of German Patent 1,274,121 (1968); (CA70: 3573v).

Dithiobenzoic acid (3.6 g), 4-vinylanisole (2.9 g) and carbon tetrachloride (20 mL) were combined and the mixture heated at 70°C overnight. The yield of 1-(4-methoxyphenyl)ethyl dithiobenzoate was 53% after purification on an aluminium oxide (activity III) column with 2% diethyl ether in n-hexane as eluent. $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.80 (d, 3H, SCHCH_3); 3.80 (s, 3H, OCH_3); 5.22 (q, 1H, SCHCH_3) and 6.88-7.97 (m, 9H, ArH).

Preparation of benzyl dithioacetate (12)

Methylmagnesium chloride (10 mL, 3M solution in THF, Aldrich) was diluted with 10 mL dry THF and the resulting solution warmed to 40°C. Carbon disulfide (2.28 g, 0.03 mole) was added over 10 minutes while maintaining the reaction temperature at 40°C. The reaction was cooled to room temperature before adding benzyl bromide (5.10 g, 0.03 mole) over 15 minutes. The reaction temperature was increased to 50°C and maintained for further 45 minutes. Water (100 mL) was added and the organic products were extracted three times with n-hexane (total 180 mL). The combined organic layers were then washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and column chromatography on a silica-gel column (Kieselgel-60, 70-230 mesh, 120g) using 500mL n-hexane followed by 5% diethyl ether in n-hexane as eluent, the pure benzyl dithioacetate was obtained as a golden coloured oil (3.0 g, 55% yield). ¹H-NMR (CDCl₃) δ (ppm): 2.90 (s, 3H); 4.46 (s, 2H) and 7.31 (m, 5H).

The following non-limiting examples demonstrate the operation of the process and the products obtainable thereby.

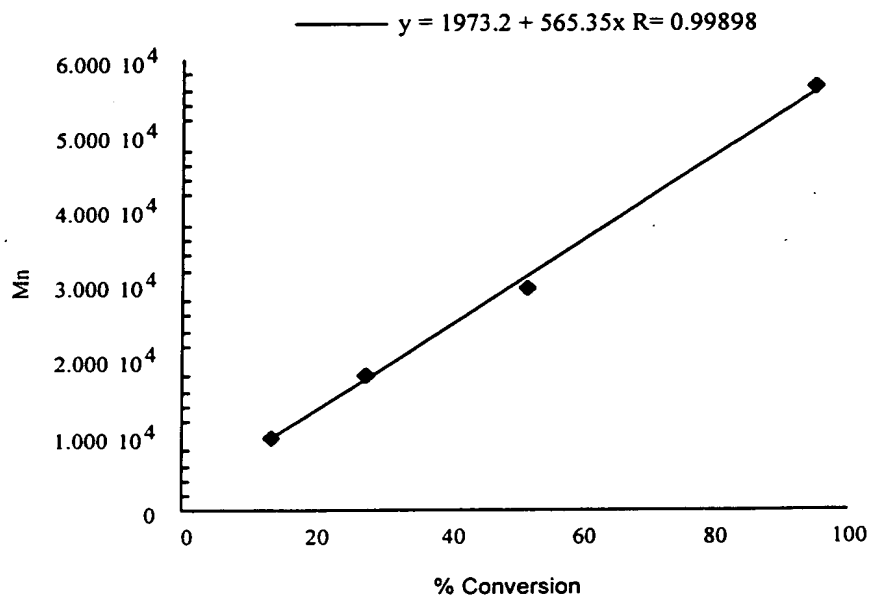
Example 1: Preparation of low polydispersity PMMA using 2-phenylpropyl dithiobenzoate

Solution polymerizations of MMA were performed at 60°C. Firstly, a stock solution containing freshly distilled MMA (15 mL), AIBN (20 mg) and 2-phenylpropyl dithiobenzoate (60.7 mg) in 5 mL benzene was prepared. Aliquots (4 mL) were removed and transferred to ampoules, degassed and sealed under vacuum. The mixtures were then polymerized at 60°C for the times indicated in the Table below. These results clearly show that the process of the invention produces very narrow polydispersity PMMA polymers. A linear plot of M_n versus % conversion is obtained which indicates the living nature of the polymerization.

Entry	time/hr	M_n	M_w/M_n	% Conv.	M_n (calc) ^a
1	2	9810	1.27	13.5	8413
2	4	18024	1.19	27.3	17013
3	8	29745	1.15	51.5	32095
4	16	56203	1.12	95.0	59205

^a M_n (Calc) = [MMA]/[dithioester] * conversion * 100.12

Mn vs Conversion of MMA Polymerization



Example 2: Preparation of low polydispersity poly(methyl acrylate) using 1-phenylethyl dithiobenzoate

Stock solution (I) of AIBN (6.6 mg) in 50 mL benzene and stock solution (II) of 1-phenylethyl dithiobenzoate (87.6 mg) in 50 mL benzene were prepared respectively. Aliquots of solution (I) (2 mL) and solution (II) (6mL) were removed and added to three separate ampoules containing 2 mL of freshly distilled methyl acrylate. The contents of ampoules were then degassed and sealed under vacuum. The mixtures were polymerized at 60°C for periods of time listed in the following Table.

Entry	time/hr	M _n	M _w /M _n	% Conv.
5	20	13452	1.11	26.2
6	64	28815	1.13	52.9
7	110	32650	1.16	63.8

Example 3: Preparation of low polydispersity poly(n-butyl acrylate) using 1-phenylethyl dithiobenzoate

Stock solution (I) of AIBN (13.4 mg) in 50 mL of benzene and stock solution (II) of 1-phenylethyl dithiobenzoate (50.6 mg) in 50 mL of benzene were prepared respectively. To a reaction vessel, solution (I) (10 mL), solution (II) (20 mL) and 20mL n-butyl acrylate were added and degassed under vacuum and subsequently the mixture was polymerized at 60°C for two hours; a very low polydispersity poly(n-BA) with M_n 33569, M_w 37771 and M_w/M_n 1.13 was obtained.

Example 4: Preparation of low polydispersity poly(acrylic acid) using 1-phenylethyl dithiobenzoate

Stock solution (I) of AIBN (6.64 mg) in 25 mL DMF and stock solution (II) of 1-phenylethyl dithiobenzoate (17.7 mg) in 25 mL DMF were prepared respectively. To a reaction vessel, 2mL of stock solution (I), 6mL of stock solution (II) and 2mL of acrylic acid (freshly distilled) were added and degassed by three freeze-evacuate-thaw cycles. The mixture was polymerized at 60°C for 4 hours. After removal of the solvent and monomer, poly(acrylic acid) (0.37 g, 17.5% conversion) was obtained. A portion was methylated (tetramethylammonium hydroxide (25% in methanol) and excess methyl iodide). GPC of the methylated sample gave M_n = 13792, M_w = 16964 and polydispersity 1.23.

Example 5: Preparation of low polydispersity polystyrene via bulk polymerization of styrene using benzyl dithiobenzoate

A stock solution of freshly distilled styrene (60 mL) and AIBN (16.9 mg) was prepared. Aliquots (5 mL) were removed and transferred to ampoules containing benzyl dithiobenzoate (11.4 mg). The ampoules were degassed and sealed under vacuum. The mixtures were then polymerized at 60°C for periods of time indicated in the Table below. The results clearly show that polymers with low polydispersity relative to the control (no benzyl dithiobenzoate; entry 8) were formed.

Entry	Time (hr)	M _n	PD	% Conv.
8 (control)	1	163 810	1.83	1.61
9	1	1497	1.36	0.68
10	2	2259	1.27	1.49
11	4	3626	1.24	3.46
12	8	6016	1.21	6.92
13	12	8892	1.16	10.60
14	16	11781	1.16	13.66
15	20	14380	1.13	17.16
16	30	18,500	1.12	22.43
17	50	25,213	1.17	31.82
18	100	33,364	1.13	42.32

Example 6: Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2-phenylpropyl dithiobenzoate

Example 5 was repeated substituting the dithioester 2-phenylpropyl dithiobenzoate (11.4 mg per ampoule). Low polydispersity polystyrene was obtained.

Entry	Time (hr)	M _n	PD	% Conv.
19 (blank)	1	285,069	1.63	1.67
20	1	833	1.12	0.49
21	4	4,511	1.09	3.74
22	20	21,478	1.14	19.45
23	50	40,007	1.17	37.49
24	100	52,313	1.18	57.33

Example 7: Preparation of low dispersity polystyrene via thermal polymerizations of styrene using 1-phenylethyl dithiobenzoate at 100°C

A stock solution of styrene (10 mL, freshly distilled) and 1-phenylethyl dithiobenzoate (24.8 mg) was prepared. Aliquots (2 mL) were added to ampoules which were degassed via three freeze-evacuate-thaw cycles and subsequently heated at 100°C. Samples were removed at the time intervals indicated in the table below and analyzed by GPC. The percentage conversion was evaluated gravimetrically. The molecular weights increased with time and low polydispersity was maintained throughout the experiments.

Entry	time/hr	M _n	M _w	M _w /M _n	% Conv.
25 (Control)	6	227,276	434,311	1.91	21.7
26	6	5 768	6 270	1.09	9.7
27	20	21 929	25 165	1.15	36.8
28	64	38 511	46 836	1.22	70.6
29	120	49 625	61 028	1.23	91.9

Example 8: Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate at 100°C

Example 7 was repeated, substituting a threefold higher concentration of 1-phenylethyl dithiobenzoate was used (75.6 mg). The results are summarized in the table below. Extremely low polydispersity polymers were obtained throughout.

Entry	time/hr	M _n	M _w	M _w /M _n	% Conv.
30	6	3439	3728	1.08	12.3
31	20	10161	11022	1.08	35.0
32	64.5	22179	24432	1.10	65.6
33	120	27008	31267	1.16	87.6

Example 9: Preparation of low polydispersity polystyrene via thermal polymerizations of styrene using 2-phenylpropyl dithiobenzoate at 100°C

Example 8 was repeated substituting the dithioester 2-phenylpropyl dithiobenzoate. The molar concentration of the dithioester the same as in Example 8 and the results are listed in the following Table.

Entry	time/hr	M _n	M _w	M _w /M _n	% Conv.
34	2	1 517	1 692	1.12	4.3
35	6	5 680	6 142	1.08	14.3
36	20	13 813	14 897	1.08	39.9
37	64	25 173	28 091	1.12	81.0
38	119	26 265	30 007	1.14	88.0

Example 10: Preparation of low polydispersity polystyrene via emulsion polymerization of styrene using benzyl dithiobenzoate at 80°C

Initial charge:	Water	75 g
	Sodium dodecyl sulfate (3% aq solution)	5 g
Initiator Feed:	4,4'-azo-bis(4-cyano-pentanoic acid)	0.209 g
	Sodium dodecyl sulfate (1% aq solution)	24 g
	(flow rate: 0.089 mL/min)	
Shot Addition:	4,4'-azo-bis(4-cyano-pentanoic acid)	0.140 g
	benzyl dithiobenzoate	0.215 g
	Styrene	3.7 g
Monomer Feed:	Styrene	32.9 g
	(flow rate: 0.20 mL/min)	

The initial charge was placed in a 5-neck, 250 mL reactor fitted with a stirrer, condenser and thermocouple and degassed under nitrogen at 80_C for 40 minutes.

The shot addition was added, and the initiator and monomer feeds were commenced at the specified rates. On completion of the initiator feed, the reaction was held at 80_C for a further 90 minutes.

Conversion 73%. The isolated polystyrene had M_n 53 210; M_w/M_n 1.37

Example 11: Preparation of low polydispersity polystyrene via emulsion polymerizations of styrene using benzyl dithiobenzoate at 80°C

When Example 10 is repeated with the exception that a higher concentration of benzyl dithiobenzoate is used.

Shot Addition:	4,4'-azo-bis(4-cyano-pentanoic acid)	0.140 g
	benzyl dithiobenzoate	0.854 g
	Styrene	3.7 g

The conversion was 19%. The isolated polystyrene had M_n 3 010; M_w/M_n 1.20

Example 12: Preparation of low polydispersity diblock poly(MA-b-EA)

A sample of poly(MA) (0.17 g, M_n 24 070, polydispersity 1.07) made using 1-phenylethyl dithiobenzoate (as described in Example 2) was dissolved in 2 mL ethyl acrylate and 8 mL benzene containing AIBN (0.52 mg). The vessel was degassed and sealed under vacuum. The mixture was polymerized at 60°C for two hours and gave a narrow polydispersity diblock poly(MA-b-EA) (0.22g, 10.8% conversion), M_n 30899, polydispersity 1.10.

Example 13: Preparation of low polydispersity diblock poly(n-BA-b-AA)

A stock solution of AIBN (6.64 mg) in 25 mL of DMF was prepared. In a reaction vessel, a sample from Example 3, poly(n-BA) (M_n 33569, PD 1.13) (0.5 g) was dissolved in 5.5 mL DMF and 4mL acrylic acid and 0.5 mL of solution (I) were added. The mixture was degassed and heated at 60°C for two hours. After removal of solvent and unreacted monomer, a low polydispersity diblock n-BA-b-AA was obtained (0.848 g, 8.3% conversion). GPC results (after methylation of the acrylic acid of the diblock): M_n 52 427; M_w 63 342; M_w/M_n 1.19.

Example 14: Preparation of low polydispersity styrene polymer using benzyl dithioacetate

A stock solution (I) of freshly distilled styrene (10 mL), benzyl dithioacetate (17.0 mg) and AIBN (2.8 mg) was prepared. Aliquots (2 mL) were removed and transferred to ampoules. The contents of ampoules were then degassed and sealed under vacuum. The mixtures were polymerized at 60°C for periods of time indicated in the table below. The results clearly show that the polydispersity of polymers formed initially (2 and 4 hours) is not as low as those prepared with benzyl dithiobenzoate, however, that of the remaining two polymers (at 16 and 40 hours) are low (1.32 and 1.24 respectively).

Entry	time/hr	M_n	M_w	M_n (calc)	M_w/M_n	% Conv.
39	2	6844	11799	1753	1.72	1.8
40	4	8565	13558	4872	1.58	5.0
41	16	18696	24686	18025	1.32	16.5
42	40	29857	36983	28157	1.24	28.9

Example 15: Preparation of low polydispersity poly(n-butyl acrylate) using benzyl dithiobenzoate

Stock solution (I) of AIBN (13.4 mg) in 50 mL of benzene and stock solution (II) of benzyl dithiobenzoate (9.62 mg) in 10 mL of benzene were prepared respectively.

Aliquots of solution (I) (2 mL) and solution (II) (4 mL) were transferred to ampoules already containing n-butyl acrylate (4mL). The contents of ampoules were then degassed

under vacuum and subsequently polymerized at 60°C for periods of time indicated in the Table below. The results clearly show that the poly(n-butyl acrylate) formed with very low polydispersity.

Entry	time/hr	M_n	M_w/M_n	M_n (calc)	% Conv.
43	2	26210	1.12	25866	11.4
44	8	91717	1.14	90760	40.0

Example 16: Preparation of low polydispersity poly(N,N-dimethyl acrylamide) using benzyl dithiobenzoate

A stock solution (I) of AIBN (2.5 mg) and N,N-dimethylacrylamide (10 ml) in benzene (50 ml) was prepared. A second stock solution (II) was prepared containing benzyl dithiobenzoate (4 mg) in 20 ml of stock solution (I). Aliquots of stock solutions (I) and (II) were transferred to ampoules (in the quantities indicated in the table below).- The ampoule contents were degassed and sealed under vacuum, and then polymerized at 60°C for one hour. The molecular weight and polydispersity data are summarised in the table below.

Entry	Solution (I) (ml)	Solution (II) (ml)	CTA (mg)	M_n	PD	M_n (calc)	% Conv.
45	0	10	2	35 057	1.14	30 266	12.9
46	5	5	1	134 532	1.23	120 597	25.7
47	7.5	2.5	0.5	224 310	1.44	293 742	31.3
48	10	0	0	832 905	2.59	-	76.9

Example 17: Emulsion Polymerization of Styrene in the presence of Benzyl dithioacetate at 80°C with SLS as surfactant and ACP as initiator

Initial Charge

Water	75 g
Sodium dodecyl sulfate (10% aq solution)	5 g

Shot Addition

<i>4,4'-azobis(4-cyanopentanoic acid)</i>	140 mg
Benzyl dithioacetate	155 mg
Styrene	3.7 g

Monomer Feed (0.2 mL/min)

Styrene	32.9 g
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Initiator Feed (0.089mL/min)

<i>4,4'-azobis(4-cyanopentanoic acid)</i>	211 mg
Sodium dodecyl sulfate (1% aq solution)	24 g

The initial charged was placed in a 5-neck reactor fitted with a condenser, stirrer and thermocouple, heated to 80°C and degassed under nitrogen for 40 minutes. The shot addition was added and the monomer and initiator feeds were commenced immediately at the feed rates specified. On completion of the initiator feed the mixture was held at 80°C for a further 90 minutes. The results of the experiment are summarized in the following table.

GPC Molecular Weight Data of PS prepared under Emulsion Polymerization conditions with Benzyl dithioacetate at 80°C with SLS.

Entry	Reaction time minutes	M_n^a	M_w/M_n	% Conversion
49	75	20590	1.27	97b
50	120	28800	1.26	98b
51	180	35220	1.33	>99
52	240	37440	1.35	>99
53	270	38420	1.34	>99
54	360	35580	1.38	>99

^a GPC molecular weight in polystyrene equivalents.

^b Instantaneous conversion (conversion of monomer added up to time of sampling).

Example 18: Preparation of narrow polydispersity block copolymers of styrene and N,N-dimethylacrylamide

The polystyrene (pSTY) (M_n 20324, polydispersity 1.15) used in this experiment was prepared by bulk polymerization of styrene (100 mL) at 60°C (30.5 hours) using AIBN (28.17 mg) as initiator in the presence of benzyl dithiobenzoate (228 mg).

The block copolymerization of pSTY and N,N-dimethylacrylamide was carried out as follows: pSTY (0.2 g), N,N-dimethylacrylamide (2 mL) and AIBN (0.5 mg) were dissolved in benzene (8 mL) in an ampoule. The resulting mixture was degassed and then heated at 60°C for one hour. After this time, all the volatiles were removed under reduced pressure and a narrow polydispersity block poly(styrene-*b*-dimethylacrylamide) was isolated (0.4g, 10.4% conversion, M_n 42955 and polydispersity 1.24).

Example 19: Preparation of low polydispersity block copolymers of styrene and 4-methylstyrene

The polystyrene (pSTY) (M_n 20324, polydispersity 1.15) used in this experiment was prepared as described above. The block copolymerization of pSTY and 4-methylstyrene was carried out as follows: pSTY (0.5 g), 4-methylstyrene (2 mL) and AIBN (2.5 mg) were dissolved in benzene (0.5mL) in an ampoule. The mixture was degassed and heated at 60°C for three hours. Volatiles were removed under reduced pressure to give a low polydispersity block poly(styrene-*b*-4-methylstyrene) (0.81g, 17.1% conversion, M_n 25380 and polydispersity 1.19).

Example 20: Preparation of low polydispersity block copolymers of methyl methacrylate and styrene

The block copolymerization of PMMA and styrene was carried out as follows: The PMMA (1.7 g, M_n 17408, polydispersity 1.20) was first dissolved in ethyl acetate and transferred to an ampoule, then the ethyl acetate was removed under reduced pressure. AIBN (2.82 mg) and freshly distilled styrene (10 mL) were added to the ampoule. The mixture was degassed, sealed under vacuum and heated at 60°C for 20 hours. After removal of the unreacted styrene in vacuo a very low polydispersity block poly(MMA-*b*-STY) obtained. M_n 35 339; M_w 43 996 ; M_w/M_n 1.24.

Example 21: Preparation of low polydispersity poly(n-butyl acrylate) via the solution polymerization of n-BA at 90°C in the presence of 1,4-bis-(dithiobenzoylmethyl)benzene

A stock solution (I) of Vazo-88 (8.03mg) in benzene (10 ml) was prepared.

Aliquots (1 mL) of stock solution (I) were added to each of a series of ampoules containing 4 mL of freshly distilled n-butyl acrylate monomer, 1,4-bis-(dithiobenzoylmethyl)benzene (12.7 mg) and 5 mL of benzene. The contents of the ampoules were degassed (three freeze-thaw cycles), sealed under vacuum and heated at 90°C for the times given in the table below.

Conversion was determined from the mass of polymer remaining after removal of the unreacted monomer in vacuo. The polymer was characterized by GPC. The results are summarized in the table below.

Entry	time (h)	M_n	M_w/M_n	M_n (calc)	% Conv.
55	1	5086	1.21	5079	4.4
56	5	56865	1.32	65571	56.8

Example 22 : Preparation of low polydispersity poly(n-butyl acrylate) via the solution polymerization of n-BA at 90°C in the presence of 1,4-bis-(dithiobenzoylprop-2-yl)benzene

Two stock solutions were prepared: stock solution (I) of Vazo-88 (10.09 mg) in benzene (25 mL), and stock solution (II) of 1,4-bis-(dithiobenzoylprop-2-yl)benzene (175.1 mg) in benzene (25 mL). Aliquots of stock solution (I) (2 ml) and stock solution (II) (4 mL) were added separately to each of a series of ampoules containing 4 mL of freshly distilled n-butyl acrylate monomer. The contents of the ampoules were degassed by three freeze-thaw cycles and sealed under vacuum. The degassed ampoules were heated at 90°C for the periods of time shown in the table below.

Conversion was determined from mass of polymer obtained after removal of all the volatiles. The polymer was characterised by GPC. The results are summarized in the table below.

Entry	time (h)	M_n	M_w/M_n	M_n (calc)	% Conv.
57	5	937	1.13	952	1.6
58	16	28035	1.21 ^a	27365	46.0
59	42	40822	1.37 ^a	43904	73.8

^a trimodal molecular weight distribution

Example 23: Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 100°C in the presence of hexakis-(dithiobenzoylmethyl)benzene

A stock solution (I) of freshly distilled styrene (10 mL, 9.09 g) and hexakis-(dithiobenzoylmethyl)benzene (48.9 mg) was prepared. Aliquots of stock solution (I) (2 mL) were added to each of a series of ampoules. The contents of the ampoules were degassed (three freeze-thaw cycles), sealed under vacuum and then heated at 100°C for the times given in the table below.

Conversion (%) was determined from the mass of polymer obtained after removal of the unreacted monomer in vacuo. The polymer was characterised by GPC. The results are summarized in the Table below.

Entry	time (h)	M_n^+	M_w^+	M_n (calc)	M_w/M_n^+	% Conv.
60	6	1352	1529	-	1.13	0.33
61	20	34098	46531	51280	1.36	27.5
62	64	79565	133435	134448	1.67	72.1

+ M_n, M_w determined by GPC, Polystyrene equivalent

Example 24: Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 100°C in the presence of 1,2,4,5-tetrakis-(dithiobenzoylmethyl)benzene

A stock solution (I) of freshly distilled styrene (10 ml, 9.09g) and 1,2,4,5-tetrakis-(dithiobenzoylmethyl)benzene (54.5 mg) was prepared. Aliquots (2 mL) of stock solution (I) were added to each of a series of ampoules. The contents of the ampoules were degassed (three freeze-thaw cycles), sealed under vacuum and heated at 100°C for the times given in the table below. The degree of conversion (%) was determined from the mass of polymer obtained after removal of the unreacted monomer in vacuo. The polymer was characterised by GPC. The results are summarized in the table below.

Entry	time(h)	M_n^+	M_w^+	M_n (calc)	M_w/M_n^+	% Conv.
63	6	989	1 096	-	1.11	0.88
64	20	25 884	31 097	27 257	1.20	22.0
65	64	67 588	87 654	90 814	1.30	73.3

+ M_n, M_w determined by GPC, Polystyrene equivalent

Exmple 25: Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 120°C in the presence of 1,2,4,5-tetrakis-(dithiobenzoylmethyl)benzene

A stock solution (I) of freshly distilled styrene (10 ml, 9.09g) and 1,2,4,5-tetrakis-(dithiobenzoylmethyl)benzene (54.5 mg) was prepared.

Aliquots(2 mL) of stock solution (I) were added to each of a series of ampoules. The contents of the ampoules were degassed(three freeze-thaw cycles), sealed under vacuum and then heated at 120°C for the times given below. The degree of conversion (%) was determined from the mass of polymer obtained after removal of the unreacted monomer in vacuo. The polymer was characterised by GPC.

The results are summarized in the table below.

Entry	time (h)	M_n^+	M_w^+	M_n (calc)	M_w/M_n^+	% Conv.
66	6	42571	54932	51416	1.29	41.5
67	20	75448	108810	100353	1.44	81.0
68	64	79845	119034	109770	1.49	88.6

+ M_n, M_w determined by GPC, Polystyrene equivalent

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

18 July, 1996

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by their Patent Attorneys

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